INNOVATIVE MULTIPHASE NANOPARTICLE COMPOSITES DEVELOPED USING ELECTROPHORESIS AND ELECTROMIGRATION

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ABSTRACT

Electrokinetic material fabrication techniques such as electrophoresis, electro-osmosis or ion transport, have been useful in constructing layered composites on electrically conductive substrates. These techniques have been widely used in producing, consolidating or cementing nano-particulate phases in uniform layers. Research is being undertaken on using these electro-deposition techniques to produce fine scale changes laterally across a surface. The goal is to develop approaches to creating novel composite surface that can have unique chemical and physical properties that cannot be obtained using conventional layered construction techniques.

1. INTRODUCTION

Composites are fabricated by adding a reinforcing material (typically a fiber or a laminar element such as fabric) into a matrix material and bonding the two materials together. Classical composite manufacturing techniques involve mixing a solid reinforcement element with a fluid matrix and curing the matrix surrounding the reinforcement (similar to the way fiberglass assembled). More recently novel techniques has been developed which use an electrokinetic approach to introduce a variety of nano-particulate materials into porous substrates. Electrophoresis cells, have been built to manufacture specially modified ceramics (Boccaccini et al., 2006). Figure 1 shows a schematic of an electrophoretic deposition system for use in infiltrating porous materials like ceramics to produce specific spatial distributions of microstructure or composition.

Electrophoresis techniques depend on using a potential field to move charged particles that are suspended in a fluid phase. In most cases the thickness of the particle layer is governed by the conductivity of the infiltrated material as the accumulation of particulates in pore spaces reduces the movement of electrons. Fabrication generally involves a second step that fixes the infiltrated particles together and bonds them to the surrounding surfaces. In the case of infiltrated ceramics or metal fibers; the deposited cake of particulates can be heated to fuse the electrophoretically-transported material into the structure.

Electrophoresis has been widely used to build up complex composites or functionally graded materials by infiltrating hard particulate phases such as zirconia or tungsten carbide into porous ceramics (Van der Biest and Vandeperre, 1999; Anne, Vleuglel, and Van der Biest, 2006). Varying the physical properties on a fine scale can be useful in distributing stress in a manufactured part.

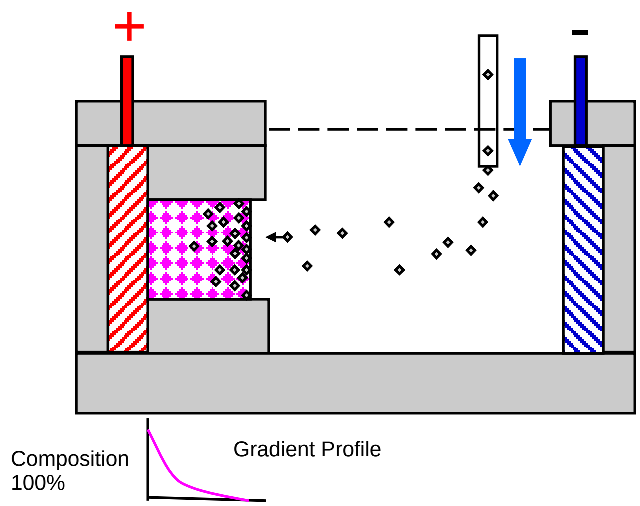

Fig. 1. Cell for elecrorphoretic transport of particles into porous solid to form functionally graded composites.

Electro-transport and electrodeposition techniques have been used to infiltrate materials other than ceramics. Electrophoresis is used to improve Portland cement-based concretes or mortars by transporting nano-particles into pore spaces (Cardenas and Struble, 2006). Ryu and Otsuki, (2002) summarize the literature on the use of chemical electrodeposition for in-filling fractures in reinforced concrete.

Electrophoresis can also be used to deposit a uniform coating over a conductive substrate such as metal, or a conductive non-metal (graphite). If the particulates being migrated are surface charged non-conductors, the deposition process is self-limiting since the resistance of the layer of particulates builds up to halt current flow and hence particle migration. When suspensions of enameling frit are used, a layer of glass particles can be built up that can be fused into a tightly bonded vitreous coating.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
DEC 2008	**N/A**	**-**

4. TITLE AND SUBTITLE
Innovative Multiphase Nanoparticle Composites Developed Using Electrophoresis And Electromigration

5a. CONTRACT NUMBER
5b. GRANT NUMBER
5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER
5e. TASK NUMBER
5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
US Army Engineer Research and Development Center, Construction Engineering Research Laboratory, Champaign, IL 61820

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES
See also ADM002187. Proceedings of the Army Science Conference (26th) Held in Orlando, Florida on 1-4 December 2008, The original document contains color images.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**UU**	**4**	

Electrophoresis has been particularly important in enameling because it can deposit a glassy frit layer uniformly on sheet metal that has a complex shape (Yatsenko, Selivanov, and Shchepeleeva, 2004). Electrophoretic deposition can produce a remarkably homogeneous and uniformly thick layer of glass frit that is difficult to obtain by dripping or spraying. Firing the coating fuses the silicate to the metal to produce a uniform, brittle coating over the metal. Normally the firing would be the end of the surface fabrication process.

The new process that is being investigated produces controlled opening in the insulating layer (glass) on the metal and uses electrotransport or electrophoresis to introduce a second phase into the surface and brings into close contact, the conductive substrate and the two electro-transported phases above it.

If the conductive substrate is a flexible or ductile material and the initial coating is brittle, as in the case of vitreous enamel over steel; the metal can be bent or stretched into a desired shape. The shaping operation fractures the brittle coating exposing the metal surface. If a rigid substrate such as cast metal or graphite is used, the conductor can be exposed by cleaving the brittle coating and etching away the coating chemically. A third material such as a plating metal or a nano-particle frit can be transferred to the fractures in the non-conducting coating using an electrical transfer system such as solution plating (or electrophoresis for organic or inorganic particulates). The new three-part composite can be fired or baked to fuse the three elements together. Composites can be created with specifically tailored thermal, mechanical and electrical properties to meet the diverse demands for materials used in Army weapons, equipment and facilities.

The basic procedure involving producing a ductile material with a brittle coating, shaping the coated material to produce fractures and introducing a third structural element to lock in the new shape is a very versatile approach. The characteristics of the infilling material can introduce new properties to the composite. A soft metal plating may allow deformation with controlled resistance. Particles of elastomer can be introduced into fractures by electrophoresis to produce a lower degree of resistance to deformation.

Multiple fracture-and-fill procedures can be used to produce a complex composite that has as unequal resistance to deformation depending on the orientation from which the deforming stress is applied. The variety of metals, ceramics, and polymer materials makes it possible to produce a broad array of unusual composites.

The development of coat-and-fracture composites also produces unusual surface properties (such as electrical or thermal conductance). The unmodified fractures represent a very narrow opening that provides a space suited to the placement of nano-meter-sized metal layers, or organic or inorganic nano-particles that can be electrodeposited. Chemical etching can be used to widen the fractures and produce wider spaces of infilling material.

2. EXAMPLE OF LATERAL COMPOSITE PRODUCTION

Samples of mild steel sheet with a porcelain enamel coating were cut into strips to examine the ability to deposit metal through openings in the coating. The sheet steel was 0.7 mm thick with a 0.15 mm-thick layer of porcelain. Test strips were prepared by using a corundum blade to cut rectangular pieces that were 7.5 mm wide and approximately 60 mm long. A polymer coating was applied to the reverse side of the metal to provide an electrical insulator.

Each test strip was bent over a mandrel to produce a series of closely-spaced, fine fractures in the enamel surface (Fig. 2).

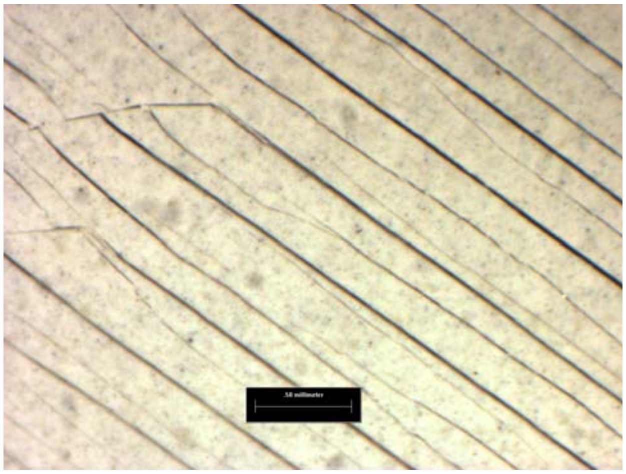

Fig. 2. Surface of enamel steel sheet showing the array of fine cracks in the enamel.

Copper metal was deposited on the exposed steel using a mechanically agitated, acid copper sulphate-based plating bath (Snyder, 2008).

The surface morphology of the test samples was characterized as using optical microscopy. The optical imaging was done using a Nikon SMU-Z binocular microscope equipped with a CoolSNAPpro digital image acquisition system (Media Cybernetics) and a Zeiss Discovery V20 stereomicroscope using the Image-Pro Plus processing and analysis software.

Figures 3 and 4 shows a three-part composite prepared using the fracture and plate process. The exposed copper metal can change both the thermal and the electrical properties of the surface. The after cleaning and drying the electrical conductivity of the new surface was verified using an ohm-meter equipped with a needle probe.

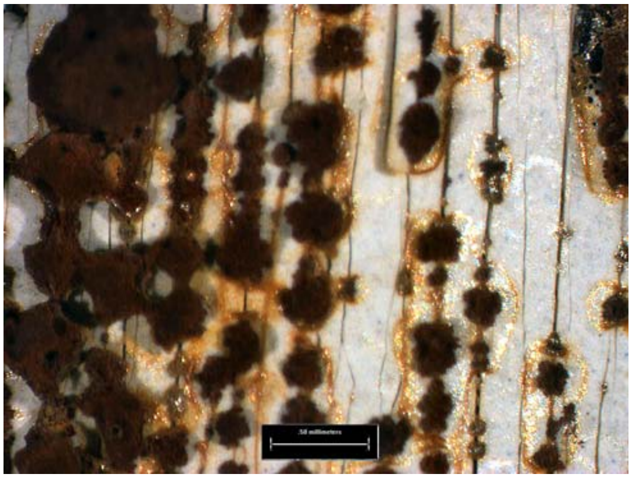

Fig. 3. Photomicrograph showing copper metal crystalline growing through the cracked glass surface.

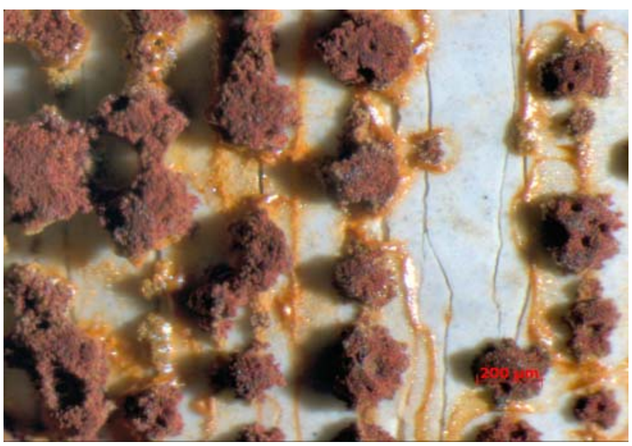

Fig. 4. Detail of the lower right field of the image in Figure 3 made using the *"bright field extended focus"* system. Note the stalk-like crystal growth produced by rapid plating rate.

3. POTENTIAL FUTURE APPLCIATIONS FOR LATERAL VARYING COMPOSITE SURFACES

3.1 Custom Shaping of Metal Surfaces

Initial efforts indicates that it should be possible to custom shape a composite by applying a vitreous enamel frit over mild steel and firing the frit to form a tightly bonded enamel. The coated metal strip is then bent into a new shape. The shape can be fixed by plating copper or another metal onto the exposed metal at the bottom of the fractures. The build up of plated metal wedges the fractures open. Refiring the enamel can fuse the metal into the enamel to form a unique triple composite of glass and plated metal over steel. Similar shaping should be possible using electrophoresis to move glass frit into fractures and fusing the glass into the existing vitreous enamel. Organic polymer nano-particles could also be electrophoretically inserted into openings in the glass coating to provide more resilient layer.

3.2 Altering the electrical characteristics of a surface

The ability to add an array of electrical conductors to an insulating surface offers the possibility of creating a composite that can be used to dissipate surface charges. As an alternative non-metallic conductive elements, such as graphite, could be migrated into cracks using electrophoresis to provide a non-corroding conductor.

3.3 Providing corrosion protection.

Sacrificial metals can be added to an enamel surface, to make it possible to maintain the more reactive metals in a corrosion-free state. For example, a second fracture set containing zinc could protect exposed copper from oxidizing. The sacrificial metal would behave as discontinuous metal plating.

3.4 Altering Surface Chemistry

Reactive compounds inserted to a composite surface can add trace amounts of specific metals or compounds to the coating. For example, a germicidal surface can be created by plating zones of silver into the discontinuous glass surface.

3.5 Altering Surface Spectral Response

Composite surfaces can potentially provide unique spectral responses that can be distinctive or deceptive. Surfaces that are polymer, metal, non-metal (graphite), polymer and glass on a very fine scale would have unique reflective properties that might be difficult to classify using typical remote sensing capabilities.

3.5 Altering Surface Lubricity

Vitreous enameled metal surfaces typically have very low surface roughness. Lubricants such as nano-particle graphite or metal sulphide intercalated in the surface may go even further to reduce friction.

SUMMARY

The investigation of electrophoretic and electrodepositing approaches to produce unusual composites has shown the following:

a) Conventional enamel application techniques can prepare a coated metal that is suitable for a composite production system.

b) The example electrotransport system (copper electroplating) was successful in introducing metal zones into the coating.

c) The properties (in this case the electrical conductivity of the coating could be altered.

d) No special preparation of the surface of the conductive substrate at the base of the fracture was needed to produce a conductive target surface.

ACKNOWLEDGEMENTS

This investigation was undertaken as part of the 6.1 Military Basic Research Program conducted under Work Unit AT2308-44. The authors wish to acknowledge the assistance of Mr. Melvin Sykes of the Concrete and Materials Branch, US Army Engineer Research and Development Center (ERDC).

Permission to publish was granted by the Director, Geotechnical and Structures Laboratory, ERDC. Approved for public release; distribution is unlimited.

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